

IV.A MEAs and Catalysts

IV.A.1 Integrated Manufacturing for Advanced Membrane Electrode Assemblies

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Objectives

- Create improved cathode structures and catalysts for proton exchange membrane fuel cells (PEMFCs) at temperatures $<100^{\circ}\text{C}$ that allow a significant reduction of precious metal (PM) without loss in performance (target of 0.3 mg/cm^2 total PM, $0.8\text{ V @ }0.4\text{ A/cm}^2$, $0.85\text{ V @ }0.1\text{ A/cm}^2$, H_2/air , DOE conditions)
- Develop a durable membrane for fuel cell operation at higher temperature and low water vapor pressure [$>120^{\circ}\text{C}$, $<25\%$ relative humidity (RH), >5000 hours]
- Incorporate the advances of the two objectives above with advanced membrane electrode assembly (MEA) fabrication processes that are amenable to mass production

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- O. Stack Material and Manufacturing Cost

- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- Fabricate highly controlled fine gradient gas diffusion layers through machine coating methods; exploit a new structure-function approach to designing improved catalysts and catalyst alloys; combine the two to create enhanced electrode and gas diffusion layer structures
- Synthesize and evaluate small-molecule organic electrolytes to test functional groups; incorporate promising functional groups into polymeric electrolytes and evaluate
- Develop new machine-based or ion beam assisted deposition (IBAD) coating methodologies to create ultra-low-loaded PM MEAs
- Synthesize new monomers and polymers; fabricate membranes and evaluate; develop methods of increasing membrane durability at higher temperature

Accomplishments

- Synthesized an improved form of a platinum alloy whereby improvements in power density are realized through reduction of synthesis-induced contaminants, optimizing alloy phases, and maintaining crystallite size of <3.8 nm; increased the mass of catalyst made from 50 g/batch to 1 kg/batch
- Extended the fine gradient approach from the gas diffusion layer to the electrode layer with the new alloy: achieved 0.78 V @ 0.4 A/cm² and 0.85 V @ 0.1 A/cm² (0.4 mg total PM/cm² as interim goal), which represents a 43% reduction in total metal g/kW compared to benchmark at start of project
- Scaled up ultra-low-loaded anodes (<0.05 mg Pt/cm²) to stack level without loss of power
- Demonstrated proof-of-principle of achieving very low cathode PM loading (<0.06 g/cm²) through IBAD
- Four additional polymer electrolytes were synthesized with conductivity of 20-80 mS/cm at 25% relative humidity (RH), and one of them has only 55% swell
- Demonstrated a membrane sufficiently durable to last 1500 hr in a fuel cell test at 120°C with cycling to 40% RH

Future Directions

- Continue to reduce PM loading through improved fine gradients via advanced modeling and characterization at Case Western Reserve University
- Construct fine gradient assemblies entirely with machine processes; scale to stack size (>225 cm²)
- Increase power density of IBAD approach by creating three-dimensional cathode structures
- Having identified good catalyst and electrode structure, begin durability testing
- Improve synthesis of candidate polymer electrolyte AE to allow immobilization and demonstrate thermal stability of candidate polymer electrolyte BA

Introduction

Continuing challenges for PEMFC technology are reducing the precious metal loading and creating new ion exchange membranes that are capable of stable operation at temperatures exceeding 120°C and preferably 150°C. The greatest barrier to

reduction of platinum metal in the MEA is due to the cathode half reaction, which can be addressed through both improved catalysts and the electrode structure around the catalyst. Operation of fuel cells at low RH (20-30%) would allow simplification or elimination of complex humidification systems and allow stack temperatures of 100-120°C with minimal

or no pressurization. Incentives to increase the operating temperature above the current 60-80°C to 120-150°C include a) smaller radiators, b) more efficient use of by-product heat, c) faster electrode kinetics, and d) increased tolerance to CO in reformed-hydrogen feed streams. Existing membranes fail to retain water at low RH and have creep at elevated temperatures.

During this report period, we have focused on new alloy catalysts, machine-made cathode structures with improved power and reduced PM loading, and new high-temperature polyelectrolytes. Our work on new electrolytes that provide the requisite conductivity at high temperature and low RH has identified candidates with improved conductivity over the benchmark.

Approach

In the initial part of the project, we identified a series of innovative catalyst preparation techniques and described linking electrochemical activity to detailed bulk structural information derived from spectroscopic determinations. During this report period, we have extended last year's work on creating highly active platinum on carbon black to enhanced alloys with improved catalytic oxygen reduction. We have identified alloy phases that contribute to electrochemical activity and now pursue avenues to enhance these phases.

Our project proposed the "fine gradient" ELAT[®] as a new design for the gas diffusion electrode (GDE) or gas diffusion layer (GDL) that would facilitate both gas and proton transport to the catalyst. By reducing undesired variations in coating quality, we were able to create fine gradients of architectural features such as pore size distribution and hydrophobicity within the gas diffusion layer structure and, with this year's work, extend the approach into the electrode structure as well. All these structures are fabricated on a sophisticated developmental coating machine, so they are readily assessed for suitability towards high-volume manufacturing. As part of the project, we will develop and compare IBAD methods to the ink-based methods to achieve low PM loadings. Finally, the most promising structures are advanced to Nuvera Fuel Cell for short stack testing/verification.

Work on higher-temperature membranes was begun with an exploration of a wide variety of organic functional groups in small molecule electrolytes for their ability to conduct protons at low RH. The more promising ones were then incorporated into candidate polymer electrolytes. During this report period, the primary focus was on bringing three desired membrane properties—conductivity, thermal stability, and low water swell—into one membrane candidate. In addition, strategies for improving membrane durability at elevated temperature are being developed.

Results

Last year we demonstrated supported platinum catalysts that had enhanced activity for oxygen reduction due to a reduction in surface contaminants arising from the synthetic procedure, and an optimized crystallite structure. This year we applied this base condition to binary platinum alloys. A key finding was the identification of a new phase in the alloy that led directly to improved oxygen reduction. For example, single-cell tests of a MEA incorporating an alloy with this phase compared to one without this phase demonstrated a 30% increase in current at 0.8 V when operating at 3 atm with air (70°C).

However, this so-called "alloy effect" was not realized at lower operating pressures, or more importantly, was greatly diminished at currents around or greater than 0.4 A/cm². We focused on applying the fine gradient (fg) approach to designing an electrode/GDL structure that realizes the potential of the alloys. Figure 1 summarizes our efforts and compares standard gradient Pt ELAT[®] (open square), standard gradient alloy ELAT[®] (Pt:Cr) (open circle), and a tuned fine-gradient ELAT[®] alloy (solid circle). As shown in the figure, the "Pt Standard ELAT[®]" is designed for good gas transport but is limited by proton transport. The standard gradient alloy ELAT[®] has mass transport limitations, even at lower currents; however, the alloy fg-ELAT[®] demonstrates a balance of transport mechanisms with notable improvement of voltage at 0.4 A/cm². In Figure 1, the Pt and alloy ELATs are all machine fabricated; the alloy fg-ELAT[®] is partially machine fabricated. All fabrications used 0.5 mg/cm² total metal on cathode in order to demonstrate the various effects.

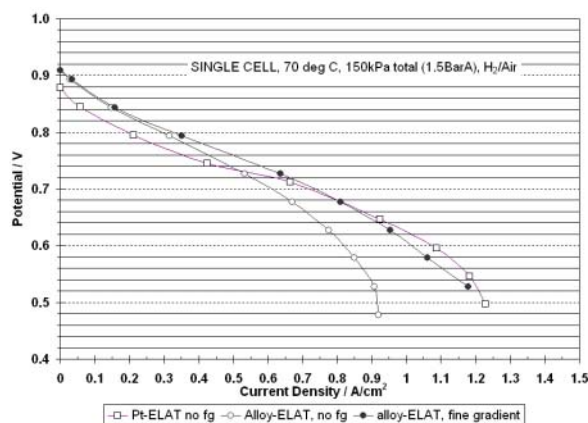


Figure 1. Single-Cell Testing of Three Cathode MEA Configurations: Standard Gradient with Pt, Standard Gradient with Pt₃Cr Alloy, and a Tuned Fine Gradient with Pt₃Cr

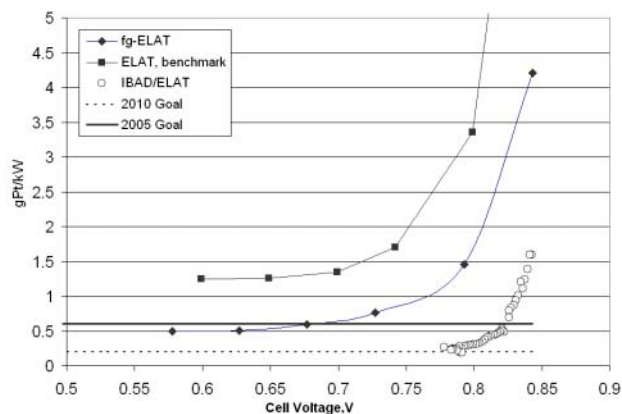


Figure 2. Platinum Specific Power (g Pt/kW) for Benchmark, fg-ELAT, and IBAD ELAT, at 80°C, 250 kPa air/H₂

The fine gradient approach was then modified to achieve 0.33 mg/cm² PM cathode loading. The trend demonstrated in Figure 1 single-cell testing has also been found in stack-level testing at Nuvera Fuel Cell.

We also applied the understanding gained from the fine gradient approach to lowering the PM content of anodes. Our team partner Nuvera Fuel Cell has shown that we can achieve 0.05 mg/cm² PM loading at the anode (H₂) in a stack without loss of power.

Another approach to lowering PM at the cathode involves IBAD. A key challenge addressed this period is creating 3-D cathode structures using ion beam deposition. Figure 2 is a plot of precious metal

specific power (grams Pt/kW) vs. cell voltage and is a useful format to gauge MEA cost. We have plotted start-of-project performance (“ELAT[®] benchmark” solid squares, 1 mg/cm² total Pt), best fine gradient to date (“fg-ELAT[®]” solid diamonds, 0.39 mg/cm² total Pt), and initial IBAD (“IBAD/ELAT[®]” open circles, 0.12 mg/cm²). The solid and dotted straight lines represent DOE 2005 and 2010 goals, respectively. Using this format, one notes the great potential of the IBAD approach to meet or exceed DOE goals. However, this promise of ultra-low PM loadings must be tempered with the realization that unacceptable power density is still limiting the approach. At DOE conditions, the IBAD MEA produces 0.79 V @ 0.1 A/cm² and 0.55 V @ 0.4 A/cm².

In the last year, four additional polymer electrolytes with low-RH conductivity of 20-80 mS/cm were synthesized (AM, AO, BA, and BB). Polymer electrolytes in this project may be divided into chemically-similar classes, for which AE and AK are closely related and AO, BG, and BA are closely related. Table 1 presents a comparison of three critical properties for these candidates – conductivity, thermal stability, and water swell.

Several candidates are acceptable in two properties; however, no candidate is sufficient in all

Table 1. Polymer Electrolyte Properties

Candidate	Conductivity at 120°C, 25% RH (mS/cm)	Upper Life Limit Kinetic TGA at 120°C (khr)	Water Swell %
NR111	11	120	50
AM	27	130	soluble
AE	73	>1,000	soluble
AK	68-156	0.005	soluble
AO	17-31	0.005	70
BG	0.4	60	25
BA	14-22	ND	55
AF	40	0.039	soluble
BB	80	0.014	soluble

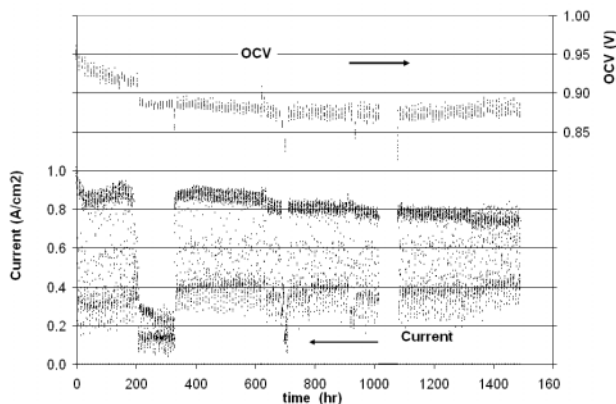


Figure 3. Current and OCV vs. Time for Membrane AV, Tested at 120°C, H₂/air, 300 kPa, Cycle between OCV and 0.5 V, with 85% RH (giving higher currents) and 40% RH (giving lower currents) (Membrane resistance was 350 mohm cm² @ 40% RH feeds)

three of these metrics. In obtaining low-RH conductivity, either thermal stability, water swelling and strength, or both have been compromised. One approach to increasing the conductivity at low RH is to increase the polarity, and hence water retention, of the polymer. In several cases this has led to water-soluble polymer electrolytes which also often have low strength. Strategies that were pursued for immobilizing and strengthening these polymers were composite membranes, improved polymerization, grafting to a high-strength substrate, and crosslinking. Attempts to immobilize AE have been unsuccessful so far; however, effort is warranted because AE has the best combination of conductivity and thermal stability of any polymer electrolyte we have examined. The mechanism for thermal instability of AO was determined, and two new monomers were designed to correct this. BG succeeded in increasing thermal stability, but at the expense of conductivity. BA still retains higher conductivity than Nafion[®], and thermal stability determination is in progress.

Membrane durability is expected to also be challenging at 120°C. A Nafion[®]/inorganic composite membrane (candidate AV) was demonstrated to have increased durability at 120°C (see Figure 3). The membrane had not failed at

1490 hr when the test was stopped, while under the same test conditions, control membranes without the inorganic portion developed catastrophic shorts near 150 hr.

Conclusions

- New alloy improvement realized over wide operating range of currents due to the fine gradient approach is being extended throughout the electrode and GDL.
- IBAD shows great potential although currently limited by low power density.
- Low loadings at the anode have been shown at stack scale ahead of schedule.
- Significantly higher low-RH conductivity than Nafion[®] is achievable, though it remains challenging to do this without compromising other properties.
- Durability of a composite membrane has improved to allow 1500 hr operation at 120°C.

FY 2004 Publications/Presentations

1. "New Catalysts and ELAT[®] Materials for Fuel Cell Applications," Emory S. De Castro, Yu-Min Tsou, Lixin Cao and Chien Hou, Fuel Cell Seminar 2003, Miami, Florida.
2. "New Catalysts and Low Cost ELAT Materials for Fuel Cell Applications," Emory S. De Castro, Yu-Min Tsou, Lixin Cao, Maria Cayetano and Hua Deng, First International Conference on Fuel Cell Development and Deployment, Connecticut Global Fuel Cell Center, University of Connecticut, Storrs, Connecticut, 2003.
3. "High Performance Oxygen Reduction Catalyst for PEM and DMFC Fuel Cells," Yu-Min Tsou, Lixin Cao, Emory De Castro, 205th Meeting of the Electrochemical Society, San Antonio, Texas, 2003.
4. "Advancement in Fuel Cell Catalysts, Gas Diffusion Electrodes, and MEAs," Yu-Min Tsou, Lixin Cao, Emory S. De Castro and Chien Hou, Fuel Cell 2004, Denver, Colorado.